

(8) E. R. Cox, *Ind. Eng. Chem.*, **15**, 592 (1923); G. Calingaert and D. S. Davis, *ibid.*, **17**, 1287 (1925).

TABLE I
ACYL DERIVATIVES OF *n*-BUTYL AND TETRAHYDROFURFURYL LACTATES^a

| Acyl deriv. | °C. | B. p., Mm. | d_{20}^4 | n_D^{20} | M^{20} | | Ester equiv. | | Analyses, % | | | |
|----------------------------|-----|---------------|------------|------------|----------|--------|--------------|--------|--------------------|----------|-------|--------|
| | | | | | Found | Calcd. | Found | Calcd. | Carbon | Hydrogen | Found | Calcd. |
| n-Butyl lactate | | | | | | | | | | | | |
| Acetyl ^b | 90 | 7.8 | 1.0036 | 1.4163 | 47.09 | 47.07 | 95.2 | 94.1 | ... | ... | ... | ... |
| Propionyl ^b | 118 | 18.7 | 0.9864 | 1.4178 | 51.65 | 51.69 | 100.9 | 101.1 | ... | ... | ... | ... |
| n-Butyryl ^b | 90 | 2 | .9731 | 1.4215 | 56.40 | 56.31 | 108.9 | 108.1 | 60.91 | 61.09 | 9.07 | 9.32 |
| n-Heptanoyl ^c | 122 | 2 | .9477 | 1.4290 | 70.27 | 70.16 | 129.3 | 129.2 | 64.84 ^d | 65.08 | ... | ... |
| n-Nonanoyl ^c | 143 | 3 | .9353 | 1.4339 | 79.70 | 79.40 | 142.3 | 143.2 | 66.92 | 67.09 | 10.05 | 10.56 |
| n-Dodecanoyl ^c | 142 | 0.6 | .9218 | 1.4388 | 93.68 | 93.25 | 163.8 | 164.2 | 69.54 | 69.47 | 11.12 | 11.05 |
| Tetrahydrofurfuryl lactate | | | | | | | | | | | | |
| Acetyl ^b | 109 | 1.2 | 1.1234 | 1.4445 | 51.18 | 51.13 | 108.2 | 108.1 | ... | ... | ... | ... |
| n-Butyryl ^b | 92 | 0.2 | 1.0768 | 1.4448 | 60.33 | 60.39 | 122.5 | 122.1 | 59.07 | 59.00 | 8.32 | 8.25 |
| n-Heptanoyl ^c | 171 | 5.4 | 1.0300 | 1.4478 | 74.38 | 74.22 | 143.1 | 143.2 | 62.89 | 62.91 | 9.14 | 9.15 |
| n-Nonanoyl ^c | 202 | 10.0 | 1.0121 | 1.4498 | 83.45 | 83.46 | 154.8 | 157.2 | 64.75 | 64.94 | 9.44 | 9.62 |
| n-Dodecanoyl ^c | 205 | 2.7 | 0.9843 | 1.4522 | 97.74 | 97.31 | 180.2 | 178.3 | 67.92 | 67.38 | 10.41 | 10.18 |

^a Acylation yields of product distilling over approximately 3° range were approximately 90% of the theoretical, except for the nonanoates (15 to 20° range). The authors are indebted to Mary J. Welsh, Mildred Gaspar and C. O. Willits for analytical data. ^b Acid anhydride used for acylation. ^c Acid chloride (Eastman Kodak Co. White Label) used. ^d Carbon determined by wet oxidation (D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, 136, [2] 509 (1940)). ^e Commercial grade of pelargonyl chloride used.

TABLE II
VISCOSITIES^a OF ACYL DERIVATIVES OF *n*-BUTYL LACTATE AND TETRAHYDROFURFURYL LACTATE

| Acyl deriv. | Viscosity at 20° | | I at 20° ^b | | I/M ^c |
|-------------------------|------------------|-------------|-----------------------|---------------------|------------------|
| | Centi-stokes | Centi-poise | Found | Calcd. | |
| Butyl Lactate | | | | | |
| Acetyl | 3.19 | 3.20 | 577.2 | 571.9 | 12.25 |
| Propionyl | 2.92 | 2.88 | 629.0 | 627.5 | 12.19 |
| <i>n</i> -Heptanoyl | 5.21 | 4.94 | 853.1 | 849.9 | 12.14 |
| <i>n</i> -Nonanoyl | 6.74 | 6.30 | 966.2 | 961.1 | 12.12 |
| <i>n</i> -Dodecanoyl | 10.84 | 9.99 | 1140.4 | 1127.9 | 12.17 |
| Tetrahydrofuryl Lactate | | | | | |
| Acetyl | 12.09 | 13.58 | 621.4 | 627.8 ^d | 12.14 |
| <i>n</i> -Butyryl | 10.30 | 11.09 | 728.1 | 739.0 ^d | 12.07 |
| <i>n</i> -Heptanoyl | 13.06 | 13.45 | 897.6 | 905.8 ^d | 12.07 |
| <i>n</i> -Nonanoyl | 17.27 | 17.48 | 1009.8 | 1017.0 ^d | 12.10 |
| <i>n</i> -Dodecanoyl | 25.03 | 24.64 | 1184.5 | 1183.8 ^d | 12.12 |

^a A.S.T.M. procedure using modified Ostwald tubes. ^b Souders' viscosity function, I (M. Souders, Jr., *THIS JOURNAL*, 60, 154 (1938); A. N. Planovskii and V. V. Kafarov, *Khimicheskaya Prom.*, No. 8, 19 (1944) (*C.A.*, 40, 2048 (1946))). ^c According to R. T. Lagemann (*THIS JOURNAL*, 67, 498 (1945)), I/M should be approximately 12. ^d In calculating I from group and structural values, -24 (recommended by Souders for 5-membered carbon rings) was used for the 5-membered tetrahydrofuran ring.

specific gravity bottle (fitted with a ground glass thermometer and cap), respectively. Viscosities (Table II) were determined by A.S.T.M. procedure,⁹ using modified Ostwald tubes and a constant temperature bath¹⁰ capable of maintaining the temperature within $\pm 0.02^\circ$ at 20°.

Determination of Boiling Water Stability.—A mixture of 5 g. of ester and 100 ml. of distilled water was refluxed for twenty-four hours and allowed to cool. Approximately 200 ml. of acetone and several drops of cresol red-thymol

blue mixed indicator¹¹ were added, and the resulting solution was titrated with 0.1 *N* sodium hydroxide. This method appeared to have certain advantages (one-phase system and less fading of end-point) over the similar method of Fordyce and Meyer.¹² Water solubilities were determined by a method similar to that of Fordyce and Meyer¹², using Sudan Red No. III dye.

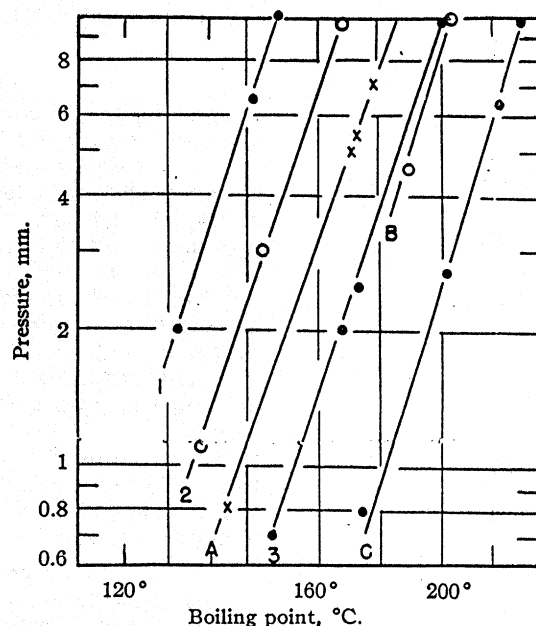


Fig. 1.—Boiling points at various pressures of acyl derivatives of *n*-butyl and tetrahydrofurfuryl lactates: acyl derivatives of *n*-butyl lactate: 1, heptanoate; 2, nonanoate; 3, dodecanoate; acyl derivatives of tetrahydrofurfuryl lactate: A, heptanoate; B, nonanoate; C, dodecanoate.

(9) A. S. T. M., D445 and Committee D-2 Report, 1936; M. R. Cannon and M. R. Fenske, *Oil Gas J.*, 33, 52 (1935); *ibid.*, 34, 45 (1936).

(10) M. L. Fein, *Chem. Analyst*, 34, 94 (Nov. 1945).

(11) A. Kleinzeller and A. R. Trim, *Analyst*, 69, 241 (1944).

(12) C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, 32, 1053 (1940).

TABLE III
PROPERTIES OF ACYL DERIVATIVES OF *n*-BUTYL LACTATE AND TETRAHYDROFURFURYL LACTATE

| Acyl deriv. | Vapor press. at 120°., mm. ^a | Solubility in water, g./liter, less than | Boiling water stability ^b | Compatibility ^c | | | |
|----------------------------|---|---|--|---|---|---|--|
| | | | | Ethyl cellulose, 1:1 ^d | Cellulose acetate, 4:1 ^d | Cellulose acetate butyrate, 4:1 ^d | Polyvinyl chloride, 1:1 ^d |
| Butyl lactate | | | | | | | |
| <i>n</i> -Heptanoyl | 1.7 | 0.07 | .. | C | I | C | C |
| <i>n</i> -Nonanoyl | 0.7 | .03 | 12.3 | C | I | CI | C |
| <i>n</i> -Dodecanoyl | .15 | .04 | 7.8 | C | I | CI | C |
| Tetrahydrofurfuryl lactate | | | | | | | |
| <i>n</i> -Heptanoyl | .34 | .16 | .. | C | I | C | C |
| <i>n</i> -Nonanoyl | .22 | .04 | 8.9 | C | I | C | C |
| <i>n</i> -Dodecanoyl | < .1 | .04 | 5.0 | C | I | C | C |

^a Estimated from Fig. 1 by extrapolation; vapor pressure of butyl phthalate at 120° = 0.26 mm. (ref. 7). ^b Volume 0.1 *N* sodium hydroxide (ml.) to neutralize sample (5 g. in 100 ml. of water) that had been refluxed for twenty-four hours; values obtained by this method with methyl and butyl phthalate, respectively, were 1.0 and 0.2 ml. ^c C, compatible; I, incompatible; and CI borderline compatibility (commercially available plastics used for tests). ^d Ratio of polymer to plasticizer.

Compatibilities.—The acylated lactic ester and certain commercially available resins (Table III) were dissolved in a suitable solvent (acetone for ethyl cellulose, cellulose acetate, and cellulose acetate butyrate and dioxane for polyvinyl chloride). The solution was placed in a Petri dish and covered with a watch glass, and the solvent was allowed to evaporate. The resulting film was examined to determine compatibility. The esters were recorded as being compatible (Table III) only when transparent and dry films were obtained.

Correlation of Properties with Number of Carbon Atoms

The experimental data of the present work (Tables I to III) characterize many members of two homologous series (α -carboboxyethyl *n*-alkanoates, I, and α -carbotetrahydrofurfuryloxyethyl *n*-alkanoates, II), but several members of both series were not prepared or examined. To provide methods for estimating the properties of the missing members and to facilitate comparison of the *n*-alkanoyllactic esters (Table I) with certain previously-described homologous series, relationships between physical properties and number of carbon atoms (or molecular weight) of the homologous *n*-alkanoyl lactates were developed. Instead of plotting the physical constants as such

against the number of carbon atoms and obtaining curved lines, certain functions of the properties that gave straight lines were selected. In agreement with earlier work, it was found that the straight line relationships usually were unsatisfactory for the first two or three members of the homologous series.

Boiling points at 10 mm. were taken from Fig. 1 and related¹³ to the number of carbon atoms (*x*) and molecular weight (*M*) by equations 1, 2, 3 and 4 (*T* = b.p. at 10 mm., °K.). Observed boiling points vary 2° or less from the values calculated by equations 1 and 3. In the case of equations 2 and 4, the variation is 1° or less.

$$\text{Butyl esters: } T^{\circ}10^{-4} = 0.061M + 1.96 \quad (1)$$

$$T^{\circ}10^{-4} = 0.85x + 5.8 \quad (2)$$

Tetrahydrofurfuryl esters:

$$T^{\circ}10^{-4} = 0.061M + 3.42 \quad (3)$$

$$T^{\circ}10^{-4} = 0.85x + 8.2 \quad (4)$$

Figure 2, constructed by plotting boiling points at 10 mm. of aliphatic acids¹⁴ against the boiling points of the corresponding carboboxyethyl (I) and carbotetrahydrofurfuryloxyethyl esters (II) on semilog paper, also can be used to estimate boiling points of the missing homologous esters. Boiling points (°K.) of the acids ($\text{H}(\text{CH}_2)_{x-1}\text{COOH}$) at 10 mm.¹⁴ were used also to derive equations 5 and 6. Boiling points reported¹⁴ in the literature vary 1 degree or less from the values calculated by equations 5 and 6.

$$\text{H}(\text{CH}_2)_{x-1}\text{COOH: } T^{\circ}10^{-4} = 1.28x + 6.06$$

$$(x = 1 \text{ to } 7, \text{ inclusive}) \quad (5)$$

$$T^{\circ}10^{-4} = 0.93x + 8.60 \quad (x = 8 \text{ to } 18, \text{ inclusive}) \quad (6)$$

The boiling points of the lactic esters (I and II) are compared with those of other homologous

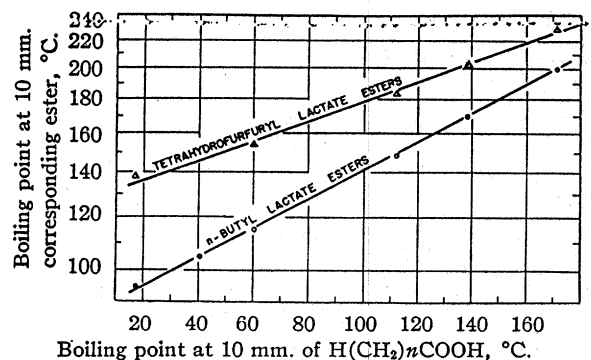


Fig. 2.—Relation of boiling points at 10 mm. of aliphatic acids and the corresponding acyl derivatives of tetrahydrofurfuryl and *n*-butyl lactates.

(13) This method for relating the boiling point at 760 mm. and number of carbon atoms or molecular weight has been used by E. Boggia-Lera, *Gazz. chim. ital.*, **29**, 441 (1899); A. H. W. Aten, *J. Chem. Phys.*, **5**, 260 (1937); and F. Klages, *Ber.*, **76**, 788 (1943).

(14) Boiling points were estimated from the vapor pressure data of W. O. Pool and A. W. Ralston (*Ind. Eng. Chem.*, **34**, 1104 (1942)) by the use of Cox charts.⁴

(21) Viscosity data of the diethyl esters were taken from R. Cedar, *Ann. Univ. Fennicae Aboensis Series*, **A2**, No. 4, 14 pp. (1926) (*C. A.*, **22**, 3137 (1928)).

equal number of carbon atoms. The lactic esters (I and II) were more viscous than the corresponding ethyl alkanoates²² and *n*-paraffins²³ (Fig. 4).

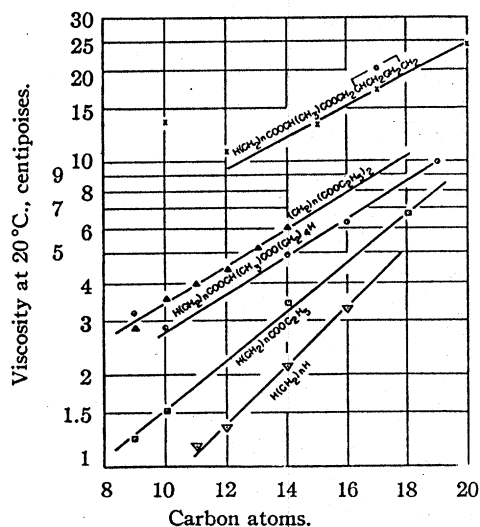


Fig. 4.—Relation between viscosity and carbon atoms of homologous compounds.

The viscosities of the *n*-butyl lactate (I) and tetrahydrofurfuryl lactate (II) derivatives are plotted in Fig. 5 as a function of the boiling points at 10 mm. The viscosities of the higher *n*-alkanoyl derivatives of butyl lactate were similar to those of the diethyl esters $((\text{CH}_2)_n(\text{COOC}_2\text{H}_5)_2)$ and *n*-paraffins of the same boiling point, but the tetrahydrofurfuryl esters (II) had viscosities considerably higher than those of the corresponding linear compounds (Fig. 5).

The values of Souders' viscosity function²⁴ were calculated (Table II) for the esters (I and II) of lactic acid; the I values calculated from the formula

$$I = \frac{M}{d} \log_{10}(\log_{10} \eta) + 2.9$$

where M = molecular weight, d = density and η = viscosity agreed moderately well with those estimated from the atomic and group increments.²⁴ In agreement with Lagemann,²⁵ the ratios between the I values and molecular refraction were approximately 12.

(22) Viscosities of ethyl *n*-alkanoates were obtained from A. E. Dunstan, F. B. Thole and P. Benson, *J. Chem. Soc.*, **105**, 782 (1914).

(23) "Landolt-Bornstein Tabellen," 3rd Supplement, p. 162, 1935, Julius Springer, Berlin; E. C. Bingham and H. J. Fornwalt, *J. Rheol.*, **1**, 372 (1930).

(24) M. Souders, Jr., *THIS JOURNAL*, **60**, 154 (1938); A. N. Planovskii and V. V. Kafarov, *Khimicheskaya Prom.*, No. 8, 19 (1944) (*C. A.*, **40**, 2048 (1946)).

(25) R. T. Lagemann, *THIS JOURNAL*, **67**, 498 (1945).

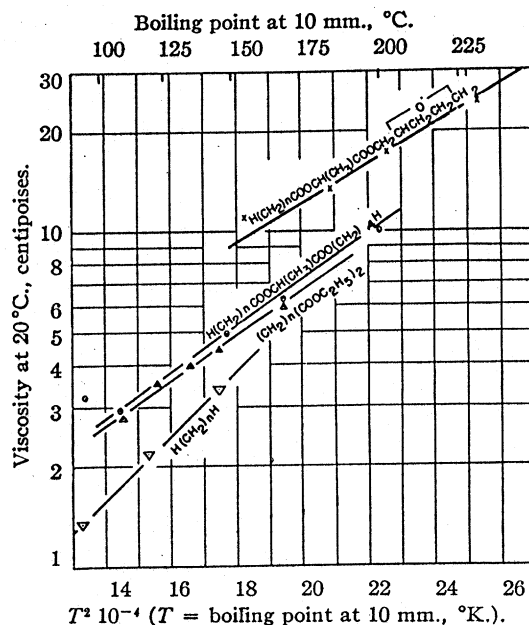


Fig. 5.—Relation between boiling points at 10 mm. and viscosity of homologous compounds.

Several of the compounds of Table I had vapor pressures (Table III and Fig. 1) sufficiently low for use as plasticizers.²⁶ The suggestion that some of the esters of the present work should be suitable as plasticizers is supported by their relatively low viscosity, moderate stability in the presence of boiling water, and compatibility with certain commercially important plastics (Table III).

Acknowledgment.—W. P. Ratchford demonstrated that the alembic type still is suitable for determining boiling points at relatively low pressures and verified the boiling points of Figure 1. The authors are grateful for this major contribution.

Summary

Several homologous *n*-alkanoyl derivatives of *n*-butyl lactate $(\text{H}(\text{CH}_2)_n\text{COOCH}(\text{CH}_2)\text{COO}(\text{CH}_2)_4\text{H})$ and of tetrahydrofurfuryl lactate $(\text{H}(\text{CH}_2)_n\text{COOCH}(\text{CH}_2)\text{COOCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{O})$ were prepared in high

yields by treating the corresponding lactic esters with acid chlorides or anhydrides. Relationships between physical properties and molecular weight are given, from which the density, refractive index, viscosity and boiling point at 10 mm. of the missing members can be calculated.

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(26) This statement is based on a comparison of the esters with *n*-butyl phthalate, a widely used plasticizer having a vapor pressure of 10 mm. at 195°.